Closure with Ecological Engineering of a Remote Cu/Zn Concentrator: Overview of 16 Years R&D Field Program

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Summary

A 16 year field investigation to apply the principles of Ecological Engineering at a small, remote mining property, containing an estimated 0.75 million tones of acid-generating tailings, is described. The rehabilitation of the site relied heavily upon the performance of a biological polishing system established in a lake, acidified during mining operations. The effluents from the mill area, the underground workings and tailings seepages represent an estimated 15 $t.y^{-1}$ of zinc and other metals in AMD, all directed into the 1 million m^3 lake. Ecological Engineering measures consisted of adding brush, phosphate, and calcium nitrate to the lake water and/or the sediments. And, since 1999, trials have been underway in the lake to determine the potential of using Mg to balance pH. The biological activity enhanced by these measures retains 80% of the zinc load within the polishing lake. The capital costs for a conventional high-density treatment plant have been estimated at $2.5 million (CDN) with annual operating costs of $0.35 million. To date, the cost of establishing a self-renewing, self-sustaining Ecologically Engineered treatment system in the lake, including all R & D, has been about $3 million.

INTRODUCTION

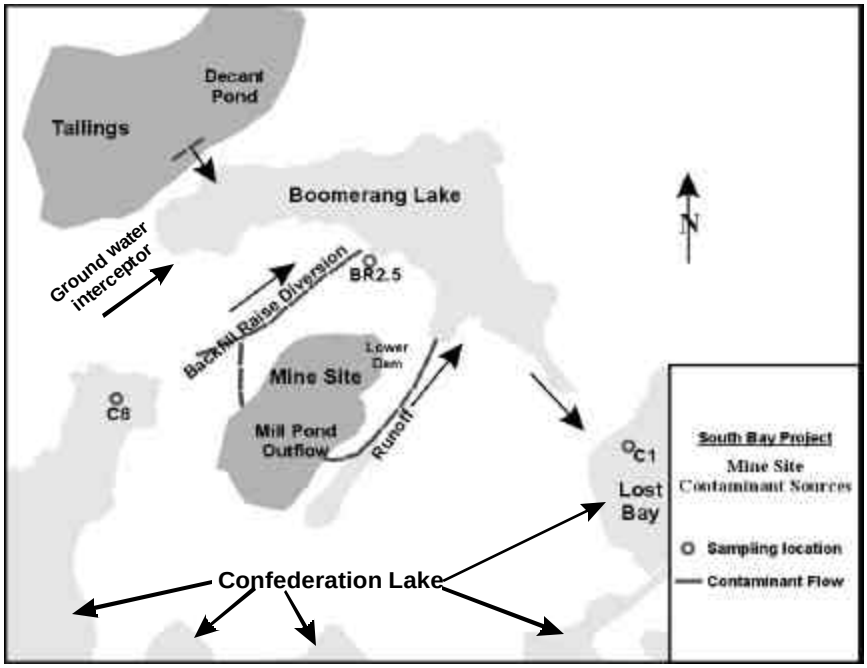
The South Bay mine and mill complex, operated from 1971 until May 1981, produced and concentrated 1,395,000 tons of ore, mostly copper, zinc and some silver (Kalin 2001). Of more immediate concern the operation also generated about 785,000 tonnes of tailings, most of which remained above ground in a tailings basin covering 23 hectares, and waste rock which was concentrated in a small pile and scattered throughout the site as construction fill, particularly on the mill complex (Kalin 2001). So, even before closure, the site was generating Acid Mine Drainage (AMD) and was expected to do so for up to 35,000 years (Kalin et al. 1992). A conventional solution, routing all run-off through a treatment plant where it could be neutralized with lime, was proposed to the company. The capital costs of such a plant, however, would have been $2.5 million while annual operating costs – in perpetuity – would have been $0.35 million. Moreover, since the site was virtually surrounded by a ring of small lakes, it would have been difficult, if not impossible, to safely store the metal-contaminated lime sludge that such a plant would have generated. Accordingly, in 1986, BP Selco commissioned an on-site research/demonstration project to explore more innovative solutions utilizing the principles of Ecological Engineering. The concept of Ecological engineering for base-metal operations is discussed in detail in Kalin 1989, Kalin 2000b, Kalin 2001, Kalin and Smith 1986, and Kalin et al. 1988.

This research has been underway ever since. Several of the most successful measures, tried and tested at South Bay, have been implemented as full-scale applications. In particular, biological polishing in Boomerang Lake has stabilized the lake and prevented the escape of contaminants downstream to Confederation Lake, an important recreational fishery lake. This paper describes the role of Boomerang Lake as a biological polishing pond. The major contaminant inputs to the lake are defined and the effects of the chemical and biological remediation measures taken are quantified.

SITE DESCRIPTION

The South Bay Waste Management Area (SBWMA) covers about 73 hectares including Boomerang Lake. The lake has a surface area of 24 hectares, a mean depth of 4.0 m and a volume of just over 1 million m^3. Because the lake is shallow, the water mixes well throughout the ice-free season. The volume of flow into the lake, of both contaminated and clean water from the entire drainage basis, is 335,500 $m^3.yr^{-1}$, resulting in a hydraulic retention time of three years. Contaminants from the site reached the lake by three distinct routes.

Mill Pond, a former catchment lagoon for the concentrator, continued to collect water, after closure from the Mill Site, where it was contaminated by contact with ore concentrates, the product of old spills, and acid-generating waste rock. The outflow from the Mill Pond follows a stream, known as the Mill Pond Run-Off, which flows through a ravine to Boomerang Lake. Seepage from the tailings, located adjacent to the lake, enters the lake directly as groundwater and by way of a groundwater interception ditch constructed in 1987. A further source of contamination was carried by water that overflowed from the naturally flooded underground workings of the mine, spilling out of the Backfill Raise. The so-called Backfill Raise Drainage Ditch was constructed in 1992, to divert this flow from Confederation Lake to Boomerang Lake.



Map 1: Contaminant Sources to Boomerang Lake

METHODS AND MATERIALS

Water Chemistry Methods

Water from all the effluent streams was sampled irregularly, depending on the time of year and financial constraints. Water samples were collected in plastic bottles and shipped in a cooler within 36 hours to the laboratory. Care was taken to maintain the redox state of water samples for field and laboratory determination of Eh. Acidity and alkalinity, pH and electrical conductivity were measured in the field and/or in the laboratory using standard methods for wastewater (Rand et al. 1976).

Acidity and alkalinity were determined using a Metrohm SM 702 Titrino Autotitrator. Redox potential (E_m) was measured using a Corning 103 meter with Fisher electrodes and then converted to E_h at standard temperature (25 ^oC). The pH was measured using a WTW 196 meter, and conductivity was measured with an Orion (WTW) Model 140 meter. Samples for heavy-metal analysis were filtered through 0.45 : m membrane filters and acidified with nitric acid to pH 2 or less before submission for chemical analysis to a certified laboratory with an Inductively Coupled Plasma Spectroscopy facility (ICP; US EPA method #200.7).

Contaminant Load Estimates

The annual precipitation records from a weather station located in Red Lake, about 100 km to the west of the mine site, were used to derive land and lake run-off estimates for the areas where either clean or contaminated water reaches the lake. The total drainage area for Boomerang Lake is 130.6 ha, of which 70 ha produce fresh, uncontaminated water to the Boomerang Lake system. In Table 1, estimated annual flows of clean and contaminated run-off are given along with the groundwater contribution from the tailings. The groundwater contribution to the lake is derived from a groundwater flow model that was constructed using Visual Modflow, a program developed by Waterloo Hydrogeologic.

Table 1: Surface water volumes of the Boomerang Lake Drainage Basin

Water Sources for Boomerang Drainage Basin		Total Runoff, ha			Flow, m^3/y
		Total	Land	Lake	
Clean	Runoff	70.0	70.0	-	192,500
Dirty	Backfill Raise (BR2.5)	12.7	12.7	-	34,788
	Mill Pond Mine Site	11.9	10.7	1.27	31,536
	Mill Pond Runoff	24.3	23.0	1.27	65,526
	Groundwater	-	-	-	22,142
Entire Boomerang Drainage Basin		130.6	107.0	23.6	335,497

Note: Clean : Dirty = 1.6 : 1

Error within estimate: +/- 1 ha

Runoff within estimated: Land: +/-2750 m^3/y; Lake: +/-1750 m^3/y

Precipitation: Land 275 mm/y; Lake: 175 mm/y

Flow measurements were carried out in the Backfill Raise Ditch, at a location where the seepage from the underground workings and the mill site combined just prior to entering Boomerang Lake. Summer measurements, projected over the entire year, reveal an annual flow as low as 4,226 m^3/y. Fall and spring flow can be as high as 103, 000 m^3/y. The average annual flow, using 56 of the measurements made between 1992 and 2002, was 28,350 m^3/y. The measured flows leaving Mill Pond, in that period, ranged between 144 m^3/y and 68,750 m^3/y with an average of 6,500 m^3/y, a value derived from 30 measurements.

These flow volumes are not consistent with estimates derived from local precipitation and run-off rates (Table1) due to the difficulty of obtaining flow measurements from the site. Efforts made to produce better measurements, by constructing weirs at Mill Pond Outflow and the Backfill Raise Ditch were defeated by erosion and debris. However, reasonable agreement between the overall water balances of the entire drainage basin and the major outflows for the entire site was derived from the groundwater model.

The effectiveness of the Ecological Engineering approach in retaining contaminants within the lake sediments was assessed by estimating the difference between the actual concentrations measured in the lake water and the estimated volumes of contaminants being delivered by the three-contaminant streams. The "Mass In" minus the "Mass Out" per annum divided by the volume of the lake, produces the estimated concentration of the metal in the lake. By comparing this estimated value with the actual measured value, we can evaluate the retention capacity of the lake as a biological polishing system.

HISTORY OF REMEDIATION EFFORTS

The first, small-scale experiments in bio-remediation at the site began in 1986 in Mill Pond with the addition of organic matter, initially sawdust and later hay. Cattails were transplanted to the periphery of the pond as well. This stimulated an algal bloom (Plate 1), which adsorbed metals from the water column. These results were sufficiently encouraging that retention dams were constructed in the Mill Pond Run-Off (Plate 2) to slow the flow of water in the ravine and promote the process of biological polishing.

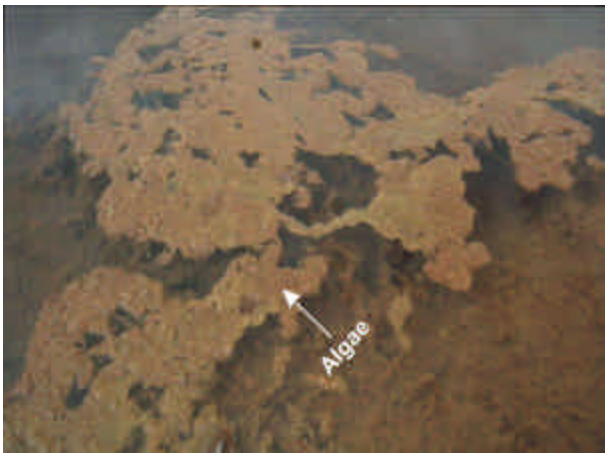


Plate 1 Algae in Mill Pond 1990

Plate 2: Mill Pond Run-Off 1988

Similarly, as the underground workings flooded and water seeped towards Confederation Lake, the Backfill Raise Diversion Ditch was constructed (Plate 3), both to lower the groundwater level and to divert the effluent to Boomerang Lake. Later in the project, the Backfill Raise Diversion Ditch was widened to provide more area for iron precipitation and metal removal. A hydrogeological investigation was initiated by the end of 1987 with the installation of 60 piezometers to define the groundwater regime in the vicinity of the tailings (Kalin et al. 1992). A diversion ditch was constructed to intercept groundwater from the tailings (Plate 4).

Plate 3: Backfill Raise Diversion Ditch 1993

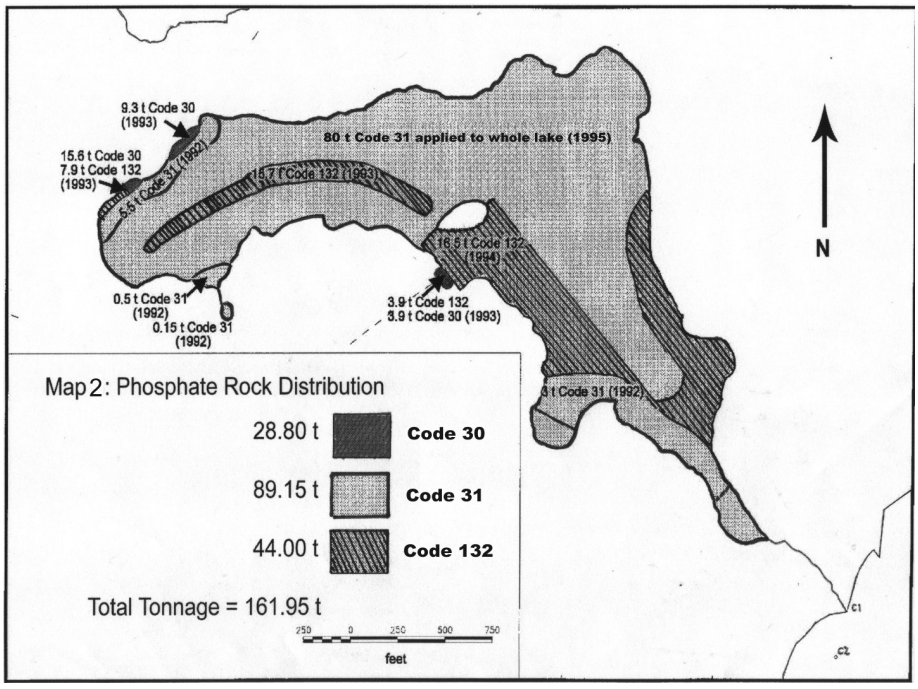

Plate 4: Groundwater interceptor ditch 1990

As the diversion ditches delivered more AMD effluents to Boomerang Lake, resulting in increased contamination and a lowered pH, it became necessary to scale up the biological polishing system in the lake. To increase the capacity of the algae and moss in the lake to sequester metals and provide alkalinity, amendments were needed. Cut brush was added to the lake (Plate 5) to provide lattices for anchorage; in 1987 and 1988, 600 cuttings were added to the shallow waters on the lake periphery; in 1990, 3,400 brush cuttings were added to the deeper water and, in 1995, 14,000 brush cuttings were added. Experiments were undertaken to determine those physical/chemical factors limiting the growth and metal sequestration by periphyton in the lake (Kalin 1998; Kalin 2000a; Kalin and Wheeler 1992; Cao and Kalin 1999).


Plate 5: Cut brush additions to Boomerang Lake 1990

Concurrent with the organic matter additions to Boomerang Lake, experiments were being conducted at other acid-generating sites with natural phosphate rock (NPR), a waste by-product of phosphate mining. Those studies indicated that NPR precipitates oxidized iron in tailings and in waste rock (Fyson et al. 1995; Kalin et al. 1998). It became apparent that the calcium carbonate in NPR released alkalinity and combined with the phosphate to immobilize oxidized iron through the formation of stable iron phosphate precipitates (Kalin and Harris 2003; Ueshima et al. 2003; Kalin et al. 2003). In 1993, in light of those findings, NPR was added to Boomerang Lake in the expectation that it would sink to the sediment and react in a similar fashion with iron on the sediment surface, a key interface associated with ferric iron hydrolysis.

After initial small-scale trials a full-scale application was carried out in l995 when 162 t. of fine, ground phosphate was added to the lake (Map 2). In 1997, one tonne of calcium nitrate was also added to correct a shortage of nitrate in the water column. The acid-tolerant moss Drepanocladus fluitans had been introduced to the lake earlier, but had never done well; with the addition of the NPR, it thrived, producing a dense moss cover above the sediment (Plate 6). This enhanced the creation of reducing conditions over the sediment, providing organic matter, excluding oxygen, and reducing the oxidation of iron accumulating as iron hydroxide in the sediments.



Although these measures reduced the burden of metals in the lake water, the increasing load of hydrogen ions from all contaminant sources needed to be addressed. After extensive consideration of many possible additions, electrochemical tests using scrap magnesium appeared the most promising. Both wood ash and limestone would become armored and sink, rendering them ineffective as a neutralizing agents. Slaked lime would react too quickly, "sterilize" the lake water and produce floc that would damage the existing periphyton protecting the sediments from iron oxidation.

Plate 6: Iron Precipitates on Moss in Boomerang Lake 2000

By comparison, magnesium consumes hydrogen as it corrodes, pulling carbon dioxide from the air, and hydrogen ions from the water forming hydroxycarbonates of calcium and magnesium which are virtually identical to the widespread and non-toxic mineral dolomite $CaMg(CO_3)_2$. It also serves in this circumstance as a cation to react with sulphate.

Moreover, magnesium corrodes completely since the process does not foul the surface of the metal. Magnesium is easily attacked by oxygen and water. With oxygen, magnesium forms white MgO, a very brittle material that turns to dust. With water, it forms $Mg(OH)_2$, a gelatinous hydroxide that in contact with air transforms into a variety of mixed oxide/hydroxide/carbonate compounds. None of these corrosion products are stable enough to prevent further corrosion, therefore no crust or oxide layer forms on the surface of the metal. It is well known that in limestone and aluminum such crust formation leads to passivation of the reactant making them ineffective as agents of neutralization.

In April 1999, eight floating rafts with 3.9 t of magnesium scrap threaded on rope and suspended from the rafts were anchored in a small bay off the entrance points for the Backfill Raise Ditch (Plate 7). The magnesium strands were enclosed with a plastic curtain to facilitate pH measurements. As it happened, the curtains inhibited the agitation of the magnesium by wave action, a key factor in reaction rates; they were therefore not used on the barges that were subsequently used to suspend open magnesium baskets. Moreover, the barges were placed in open water to expose them to agitation by waves.

Plate 7: Magnesium rafts in Boomerang Lake 2000

Plate 8: Magnesium barges in Boomerang Lake 2001

Measurements of pH in the vicinity of the Mg rafts did not show promise. The reaction of the magnesium was slow – although it is still occurring four years later. A faster reaction is expected from the Mg suspended in baskets from two barges in open water. In June 2001, a Mg barge, supporting 264 kg of Mg pieces was anchored near the Boomerang Lake outflow (Plate 8). In September 2002, an additional 138 kg of Mg pieces were added to the barge and a second barge, supporting 325 kg of Mg scraps was put into the lake. In the winter of 2002 a pH of 8 was recorded in the magnesium baskets. The effectiveness of Mg and a potential scale-up in Boomerang Lake is presently being evaluated.

RESULTS AND DISCUSSION

The contaminant load to the lake is summarized during four distinct time periods. The first phase of bioremediation efforts, to provide anchorage for algae and moss with brush cuttings, spans 1986 to 1992. The second phase was inaugurated in 1993 by the extension of the Backfill Raise Diversion Ditch, which delivered more iron to the lake, and culminated in 1995 with the full-scale application of NPR. During the period 1996 to 1999 no further measures were taken. The final phase span, 2000 to 2002, may register the effects of the Mg introduced in 1999 and the completion of Backfill Raise Diversion Ditch extension. These four time periods are considered with respect to the concentrations in estimated flows from the contaminant sources, the groundwater from the tailings, the effluent from the underground workings through the Backfill Raise Diversion Ditch, and from the mill area through the Mill Pond Run-Off (Table 1).

Metal Sources to Boomerang Lake:

The metal sources to Boomerang Lake are shown in Figure 1. For zinc, the average annual total load has more than tippled since it was first measured in 1986, increasing gradually to reach a grand total of 227 t by 2002. A gradual increase is noted from the groundwater, whereas the contribution from the Backfill Raise Diversion Ditch has decreased since 1999. Mill Pond Run-Off zinc loads have increased in the last period, due to the draining of Mill Pond. This was required to stop highly contaminated, small seepages at the mill site. The zinc load in the most recent period is 19.4 t with a distribution of 42 % from groundwater, 23 % from the Backfill Raise Diversion Ditch and 35 % entering from Mill Pond Run-Off (Figure 1).

Figure 1: Contaminant Loads to Boomerang Lake (1986-2002)

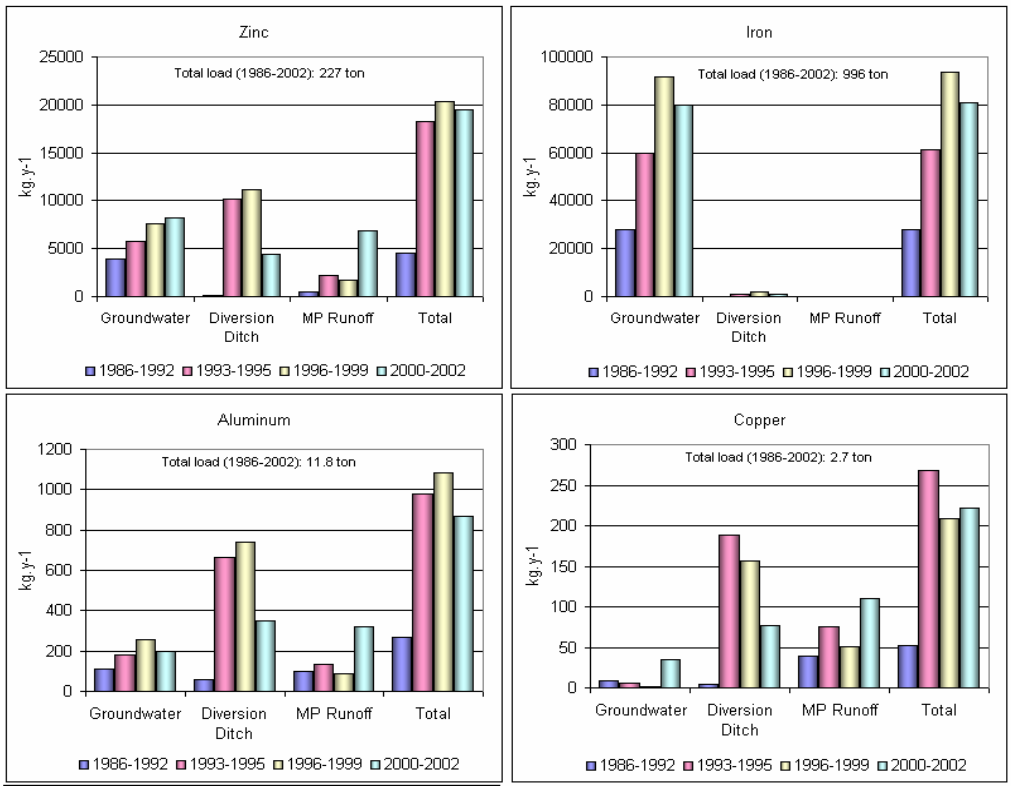


Table 2 gives the metal concentrations in the piezometers in the tailings that seep into Boomerang Lake. Piezometers (M46, M32, M9) are located on the inside perimeter of a buried concrete wall which was constructed during mine operation. Attempts have been made to grout the wall but to no avail. The geochemical reactions leading to the increase in concentrations are presently being evaluated. The large ranges of concentration are evident. The only element that shows a decreasing trend with time is Cu, whereas all other elements, Al, Fe and Zn appear not to stabilize. The amount of groundwater seepage determined by the groundwater model used to calculate the load to Boomerang Lake is 22,100 m^3/y.

Table 2: Concentrations (mg/l) for Groundwater Mass Balance

	Date	Piezo	Al	Cu	Fe	Zn
Period 1 (1986-1992)	11-Jun-86	M46	0.93	0.01	1180	187
	11-Jun-86	M32	2.3	0.01	1139	285
	11-Jun-86	M9	4.7	0.02	3436	273
	18-Jul-87	M46	3.7	0.5		98
	18-Jul-87	M9	3.4	0.2		59
	18-Jul-87	M32	3.7	0.5	289	98
	19-Jul-87	M46	9.4	0.9	289	110
	19-Jul-87	M32	3.4	0.2	290	59
	19-Jul-87	M9	9.4	0.9		110
	8-Apr-88	M9	1.6	0.09	2144	83
	8-Apr-88	M32	0.7	0.09	927	56
	8-Apr-88	M46	0.6	0.05	1304	602
	25-Mar-92	M9	24	1	1450	355
	25-Mar-92	M46	1	1	1450	139
Period 2 (1993-1995)	Average of Period 1 and Period 3					
Period 3 (1996-1999)	9-Sep-96	M9	23.9	0.1	3410	263
	9-Sep-96	M32	0.92	0.02	3470	259
	9-Sep-96	M46	8.18	0.03	6280	517
	23-Sep-96	M9	28.8	0.16	3180	252
	23-Sep-96	M32	0.25	0.03	3070	293
	23-Sep-96	M46	7.81	0.02	5400	466
Period 4 (2000-2002)	7-May-01	M32	0.8	<0.001	2640	220
	7-May-01	M46	11	<0.001	5340	680
	7-May-01	M9	21	1.1	3570	360
	7-Jul-02	M32	0.31	<0.001	2520	190
	7-Jul-02	M46	4	<0.001	5210	510
	7-Jul-02	M9	16	2	2320	270

Since 1986, 996 t. of iron has entered Boomerang Lake. The lake has also received 2.7 t. of copper, a substantial amount given the toxicity of the metal. Most of the copper currently arrives by way of the Mill Pond Run-Off (50%), the Backfill Raise Diversion Ditch (35%) and groundwater (15%). The copper loading in the Mill Pond Run-Off was due primarily to surface runoff from the old mill site area. This contribution is expected to be reduced as the mill site is remediated. (Plates 9 and 10).

Aluminum loads to Boomerang Lake have more than doubled since 1986 (Figure 1). In the most recent 3-year period, the average annual load was estimated to be 0.87 t (2000-2002). The bulk of the aluminum came from the Mill Pond Run-Off (37%) and the Backfill Raise Diversion Ditch (40%), with 23% coming from the groundwater. The total amount of aluminum that reached the lake since 1986 has been 11.8 t.

Plate 9: Mill Site before clean up 2002

Plate 10: Mill Pond drained surface after woodash 2002

Overall, recent contributions of major heavy-metal contaminants are decreasing from the Backfill Raise Diversion Ditch. Experimental applications of Mg are underway in the outflow of the Backfill Raise and in the highly contaminated seepages from the area of the former mill concentrator, but these are on such a small scale that it is unlikely that they are effecting the reduction. A more likely explanation is to be found in the draining of Mill Pond, which considerably reduced the seepage flow, and in the distribution of wood ash on the site surfaces that has promoted the growth of moss in the cracks in the rock surfaces and so minimized the infiltration of rainwater.

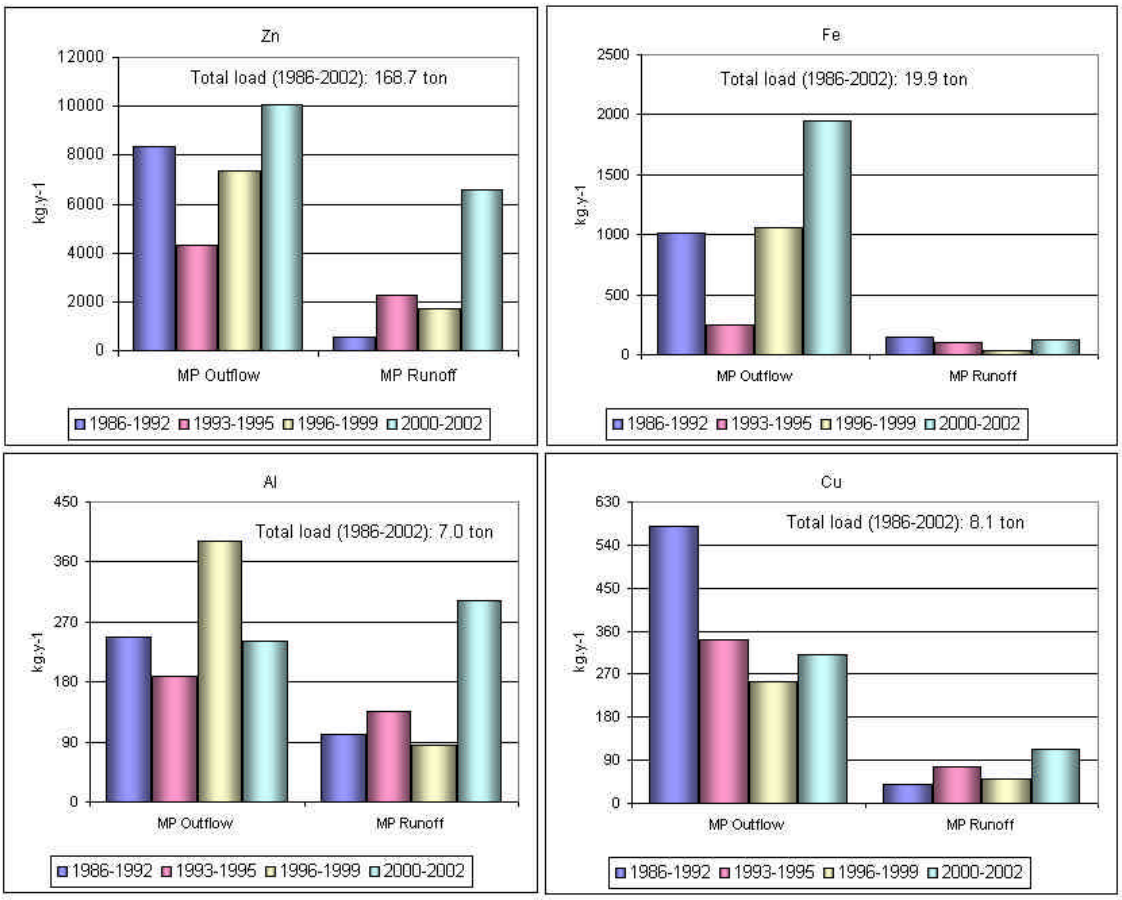
It is expected that the water quality in the Mill Pond Run-Off ravine will improve as the remediation efforts for the mill site take effect. They were completed by the end of 2002. The effectiveness of the polishing system, prior to the draining Mill Pond is evident. It appears that the copper discharged in a large pulse during the draining of Mill Pond has damaged the algae previously blooming behind the first retention structure in the ravine (Figure 1).

Figure 2 presents in more detail the metal loads for the same four time periods in the Mill Pond Outflow and compares it with the load at the two lower retention structures in the Mill Pond Run-Off ravine. The flow leaving Mill Pond is about 30,000 m^3/y which doubles to 66,000 m^3 /y by the time it reaches the lowest retention structure. In the first three periods the metal load entering Boomerang Lake from Mill Pond Run-Off is lower than that in Mill Pond Outflow; zinc by 48 to 94%, iron by 58 to 97%, aluminum by 28 to 78% and Cu by 78 to 93%. In the last period, the reductions are smaller (particularly for Zn and Al), due to the draining of Mill Pond, which affected the biological polishing system in the ravine. The system is expected to recover with time.

Metal Retention

If the concentrations of contaminant load delivered to the lake are compared to contaminant levels in the lake for each of the four phases of the remediation, a measure of removal efficiency of the biological polishing system in the lake can be established.

Figure 2: Contaminant loads at Mill Pond Outflow and Mill Pond Run-Off

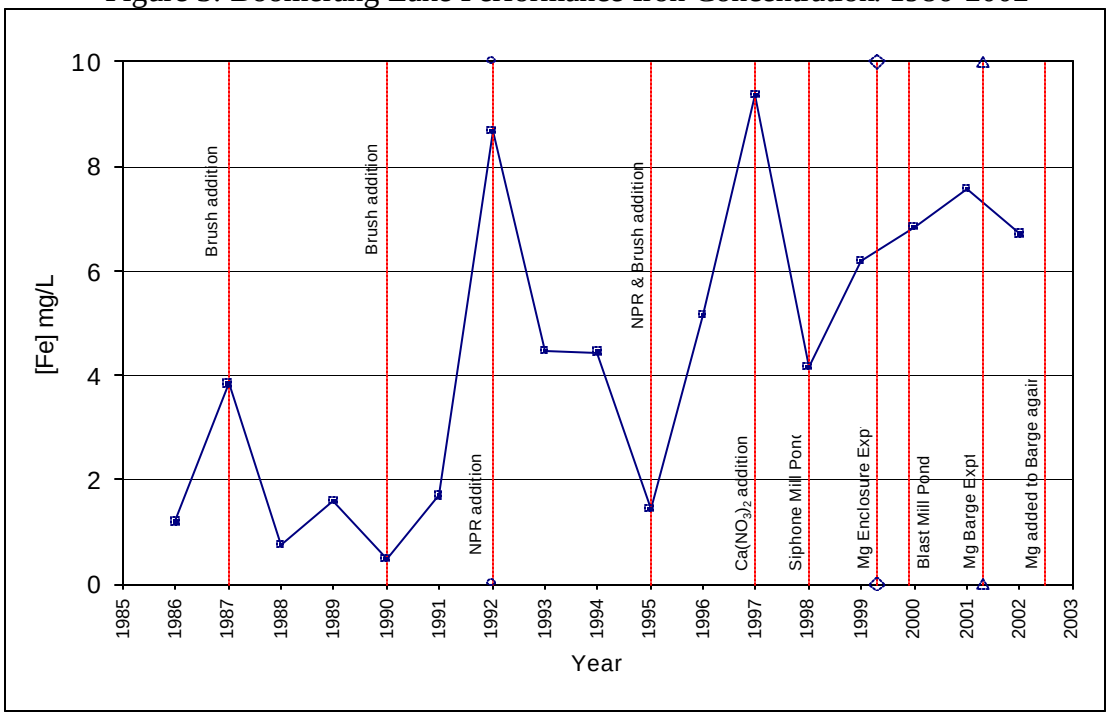


Iron: Comparisons of the expected and actual loadings of iron in the lake are not applicable since iron in the groundwater mostly precipitates as it passes through the neutral sediment. The iron that does emerge does so in a reduced form and immediately oxidizes. Since the lake water is still above the critical pH of 2.5 the oxidized iron remains in solution. As the seepage enters the lake, the iron is deposited as iron hydroxide, gradually lowering the pH of the lake. Extensive work has been carried out to quantify the iron cycling in the lake as well as the metal accumulating in the lake sediments. A complete mass balance of the particulate matter in the water and sediment layers (Kalin et al. 1995; Fyson et al. 1998) is in preparation. Figure 3 presents the concentration of iron in Boomerang Lake water from 1986 to 2002.

Measurements of the resident iron in the lake throughout the entire period 1986 to 2002 suggest that concentrations began to increase in 1990 at about the same time as brush was being introduced to the lake (Figure 3). It seems unlikely that the two events are connected. A more likely explanation is that iron was being mobilized as the result of the construction activity of the

Backfill Raise Ditch or was introduced by new seepages from the tailings. But whatever the source of the iron, it is clear that the concentrations were effectively reduced by applications of NPR. The brush enhanced the surface area for algae and moss growth and these organisms began to stabilize the sediments and remove particulate iron.

Figure 3: Boomerang Lake Performance Iron Concentration: 1986-2002



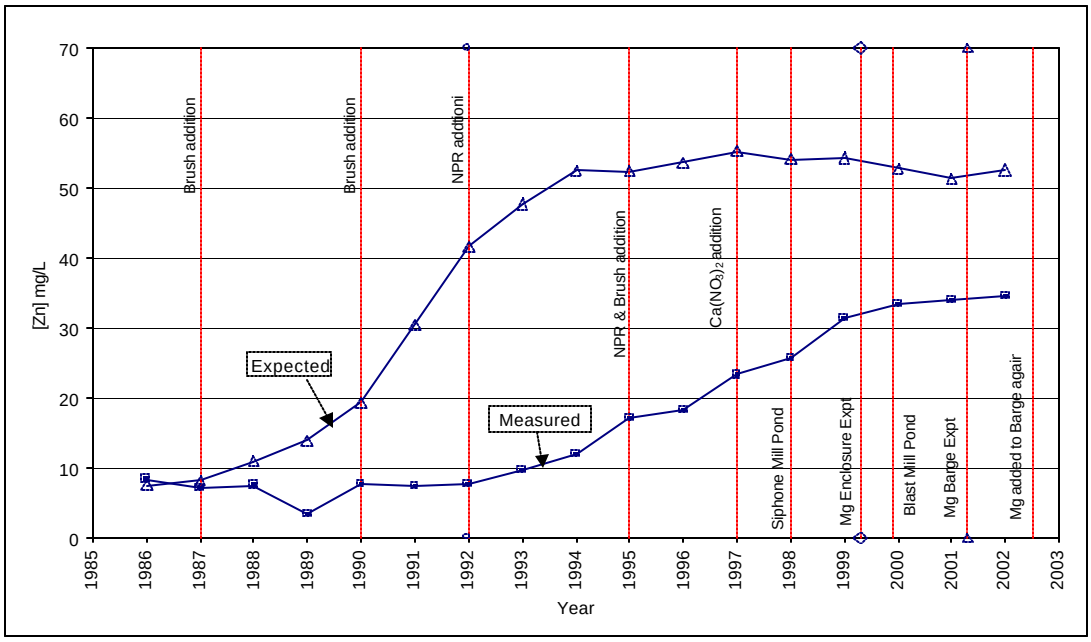
Quantification of iron precipitates formed in the open water revealed an iron deficit in the water column as expected due to the as-of-yet unquantified role of the sediments. The recent decrease may reflect the combined effect of greatly increased periphytic growth of moss and algae on the lake sediments and possibly the Mg additions. A mass balance for the metals in the biota and sediment is in preparation.

Zinc: The measured zinc concentration in the lake remained relatively constant between 1986 and 1993, varying between 8-10 mg/l while the expected zinc concentrations, based on load entering the lake increased over the same period. In other words, more zinc was entering the lake but was not reporting in the water (Figure 4).

Zinc precipitates with iron hydroxide and likely forms zinc carbonate in the sediments. It precipitates as a hydroxide at pHs between 6.5 and 7.5, whereas the current pH of the lake is around 3.0. Some of the zinc will be accounted for in the sediments, where the average concentration is 0.8%. The highest zinc concentration measured was 3.5% (n= 49).

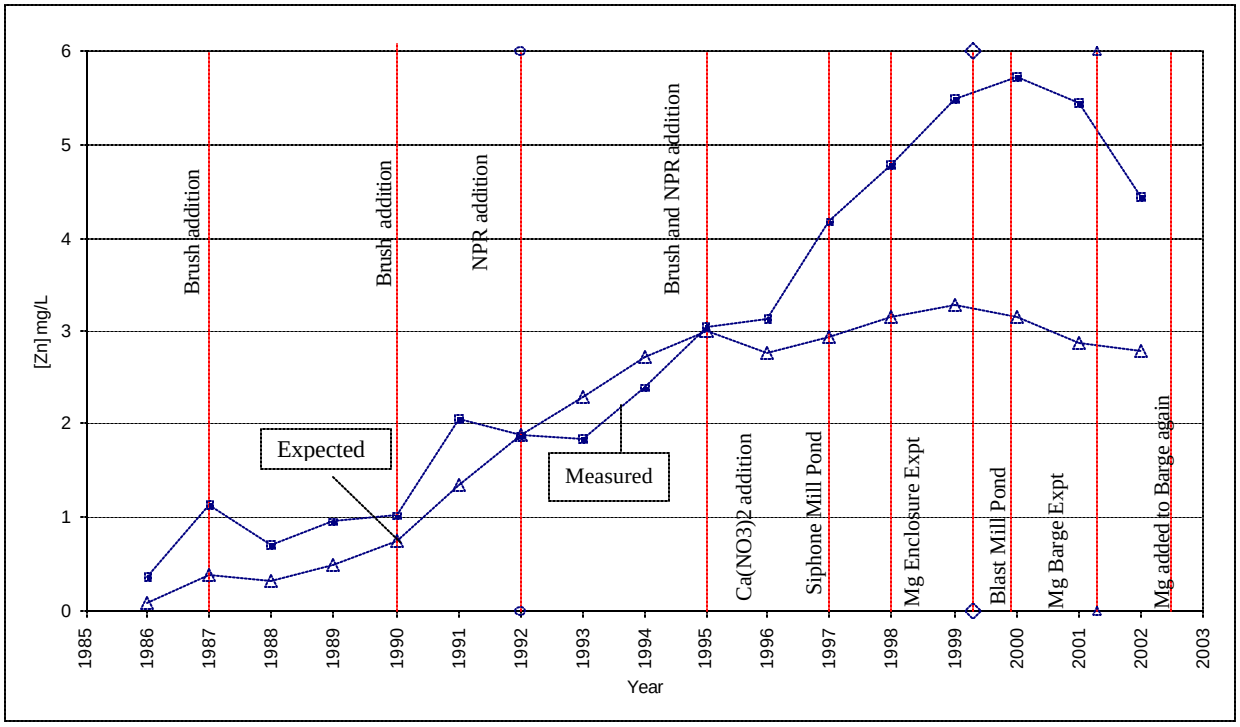
Measured zinc concentrations gradually increased from 1993 to 1999, but have since stabilized, corresponding with load reductions. It is unlikely that this is due to the Mg additions to Boomerang Lake.

Figure 4: Boomerang Lake Performance Zinc Concentration: 1986-2002



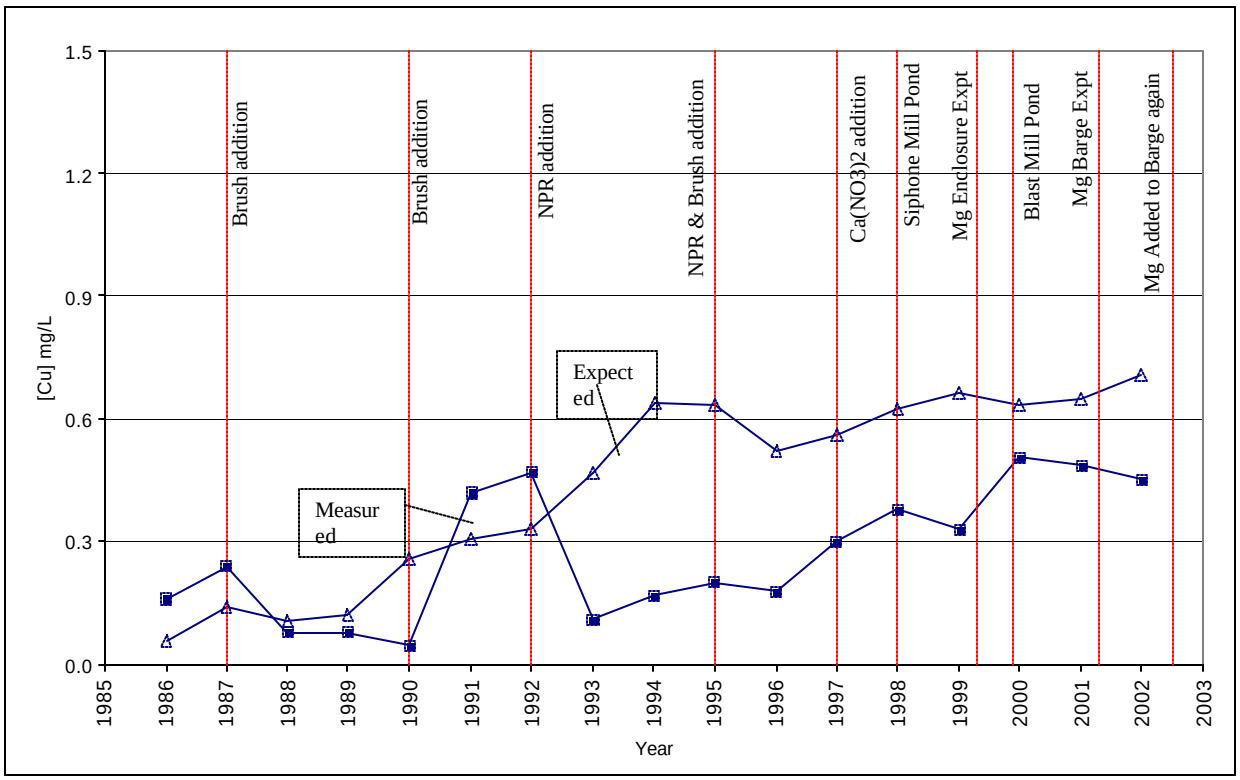
Aluminum: Expected and measured concentrations for Al are plotted in Figure 5. The measured concentration in the lake reflects the incoming loadings until 1995, at which point the lines diverge. The increase in measured concentrations suggests that the sediments release aluminum. The cause for this will be clarified when a mass balance of the solids (sediments, sedimentation traps and biota) in the polishing system is completed. Since 2000, concentrations have been decreasing, possibly due to the Mg additions.

Figure 5: Boomerang Lake Performance Aluminum Concentration: 1986-2002



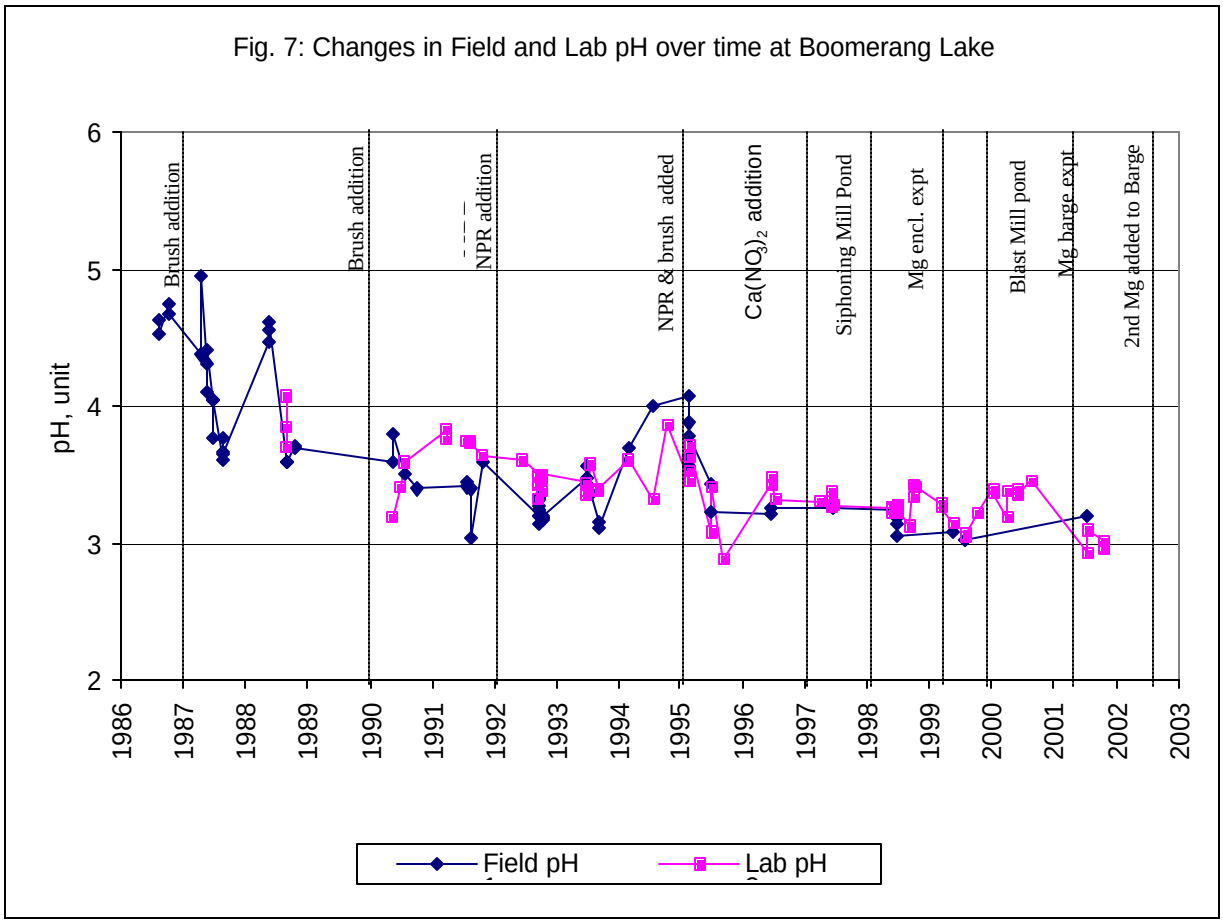
Copper: Figure 6 presents copper concentrations over the study period. For the most part, they were relatively constant for the period from 1986 to 1996, remaining around 0.2 mg/l with one abrupt increase to 0.5 mg/l in the period 1990 to 1992 followed by an equally abrupt decrease. The measured values are generally lower than expected but the two curves more closely correspond in the period 1997 to 2000. Measured concentrations since then gradually decrease.

Figure 6: Boomerang Lake Performance Copper Concentration, 1986-2002



Both the metal concentrations in Boomerang Lake and the rate of biological polishing are to a large degree determined by the prevailing pH. Figure 7 presents average pH values plotted for lake samples measured in the field and in the laboratory, generally 3 days after collection. In general, both values are in agreement. In the early years, before the biological polishing system was established, the seasonal pH trends were pronounced, reaching a peak value of 4.9 in April 1988 and a low of 3.6 in August 1988, and returning to 4.6 in May, 1989. These trends, spanning an entire pH unit, are natural due to the generation of hydrogen ions. As expected, a slight increase was noted after the first addition of phosphate to the sediments, and a larger increase, up to pH 4, after the second addition in 1995. By September of the same year the lowest pH value was measured with 2.9 but it has stabilized since that time. This is likely due to the increasing moss cover in the lake and possibly due to the magnesium additions.

Figure 7: Changes in Field and Lab pH over time in Boomerang Lake



Magnesium

It is possible to relate some of the water quality trends in Boomerang Lake to Mg, although a conclusive evaluation of both experiments in the laboratory and in Boomerang Lake is in preparation. The main attraction of this approach is that it slowly, but steadily, consumes hydrogen ions without fouling of the metal surface.

Corrosion products lightly attached to a magnesium metal surface reduce access to oxidizing agents, e.g. oxygen and/or water. The overall kinetics of Mg corrosion is a function of the accessible surface, the amount of corrosion agent available for reaction per time unit, the temperature at the corrosion site, and the activation energy of the corrosion reaction. In a general way the process may be described by a kinetic equation:

$$\frac{\partial[Mg(II)]}{\partial t} \approx F\, k\, [KP]^{v}$$

In this equation, the increase in the Mg (II) concentration with time is expressed by the accessible Mg metal surface per unit volume, a general expression of the corroding agent(s) KP, the unknown reaction order and the kinetic constant k.

The amount of surface area and the weight of Mg suspended in the lake are presented in Table 3 along with the time since exposure. From 1999 through 2002, a total of 4.6 t of Mg scrap were added, representing a total surface area of 1339 m^2. As noted above, the reaction of magnesium suspended from the first raft was slow, but is ongoing. Only the most exposed pieces on the outside of the raft have completely dissolved. The rate of corrosion was much faster in the magnesium suspended from the barge anchored in open water in the summer of 2001. By the next summer, it had completely dissolved and was replaced. Furthermore, the magnesium in the first barge, with the lowest ratio of weight to surface area, reacted most rapidly. A clearer picture will emerge, when all the magnesium is used up, probably by the summer of 2004.

Table 3: Magnesium placement in Boomerang Lake

Constellation	Date Mg added	Location in Lake	Weight kg	Surface Area m^2	Ratio kg/m^2	Status of Mg to date
Rafts	6-Apr-99	in quiet bay	3901	1047	3.73	still active
Barge 1	28-Jun-01	in open lake	264	133	1.98	used up
	20-Sep-02		138	47	2.91	still active
Barge 2	20-Sep-02	shallow water (close to outflow)	325	112	2.91	still active

The reaction order and the detailed chemical nature of the corroding agents KP are unlikely to change drastically from the tested conditions in Boomerang Lake. In the test situation where Mg scrap metal pieces are suspended in Boomerang Lake, the major corroding agent is acidic water.

The reaction order depends on the reaction mechanism and is expected to change with temperature, as well as with the concentrations of all species involved in the reaction. The reaction rate, which is affected by temperature, will be higher in summer. Also, the rafts and the barges containing the Mg scrap pieces will be moved by the waves in the summer, further increasing the reaction rates. Unfortunately the second barge was located in very shallow water, close to the outflow of Boomerang Lake, reducing its exposure to waves. The kinetic constant may be expressed by an Arrhenius-like relationship:

$$k = Ae^{-\frac{\Delta E^H}{RT}}$$

Where A is a kinetic pre-factor, E^H is the Gibbs free energy of activation; R is the gas constant and T the absolute temperature in degrees Kelvin. Hence, the kinetic factor k for a given chemical reaction depends essentially on temperature. Since temperature is seasonally changing the k varies with the season. Thus, the accessible area A has a considerable influence on the overall kinetics of the corrosion process of magnesium in water solutions, reflected by the lower

weight to surface area ratio of the scrap used up quickly in barge 1. The barge was replenished with more scrap.

Since the coatings and crusts formed on the Mg surfaces in lake waters are brittle and easily dispersed, movement of the Mg in the water, either by wind or waves, will have a strong influence on the overall reaction rate of the process. This conclusion has been confirmed by the rapid reaction of the magnesium and by the visual observation that more hydrogen bubbles emerge from the barges than the rafts; fewer but larger bubbles emerge from the magnesium raft. To determine the parameters of the above-given kinetic equations for the boundary conditions of Boomerang Lake, the data from laboratory experiments and the fieldwork were evaluated.

The k values are estimated for three sets of conditions tested in the laboratory. Magnesium surface was exposed to Boomerang Lake water both under stagnant and stirred conditions at a room temperature of 20 to 25 ^{o}C. A stagnant exposure was carried out in the refrigerator. The average k value at room temperature with stirring was 1.25×10^{-5}, and when the temperature was lowered and the conditions were stagnant, the value dropped two orders of magnitude to 1.42×10^{-7}. The value of k has the units of H^+ h/cm^2.

With these laboratory-derived k values the question could be addressed as to the apparent absence of a measurable pH increase due to the placement of Mg in Boomerang Lake. A dynamic system such Boomerang Lake, where natural fluctuation of pH can be expected, is difficult to assess, particularly at such a low pH with a large amount of hydrogen ions in solution. The amount of hydrogen ions consumed, using the surface area of Mg suspended in the experiment, is related to the surface area of the magnesium suspended from the barges and the rafts (Table 3). Using this as the basis of the estimate, the 4.6 t of magnesium added to the lake will consume 258,711 moles of H^+. Theoretically, to affect a pH increase in Boomerang Lake from 3.0 to 3.1, 258,690 moles of H^+ would have to be consumed. Using a k value an order of magnitude lower (1×10^{-6}), for the field conditions, averaging winter and summer temperatures and allowing for insufficient agitation, the expected increase of pH would be similar to the theoretical values calculated; 258,690 H^+ moles or an expected increase of 0.1 unit, which is hardly measurable.

To reach pH 4 from the present pH 3, the consumption of about 900,000 moles of H^+ would be required. The overall goal is to estimate the amount of Mg metal necessary to achieve controlled increase in pH in Boomerang Lake. With the present information available it is estimated that, to raise the pH to 4, assuming a similar weight of surface/area ratio of magnesium, will require about 16 t of Mg scrap. This is a preliminary estimate and will be reassessed after all or most of the Mg in the lake has been consumed.

Figure 8 presents the magnesium load to the lake. As with iron, the largest contribution is delivered by groundwater. The Backfill Raise Diversion Ditch and Mill Pond Run-Off contribute less although the load from both has recently increased due to experimentation with highly contaminated seepages in both drainage areas (Plates 11 and 12).

Concentrations of magnesium in Boomerang Lake have increased and are currently stable at about 18 mg/l. This is not clearly in response to the Mg addition (Figure 9).

Figure 8: Mg Loads to Boomerang Lake

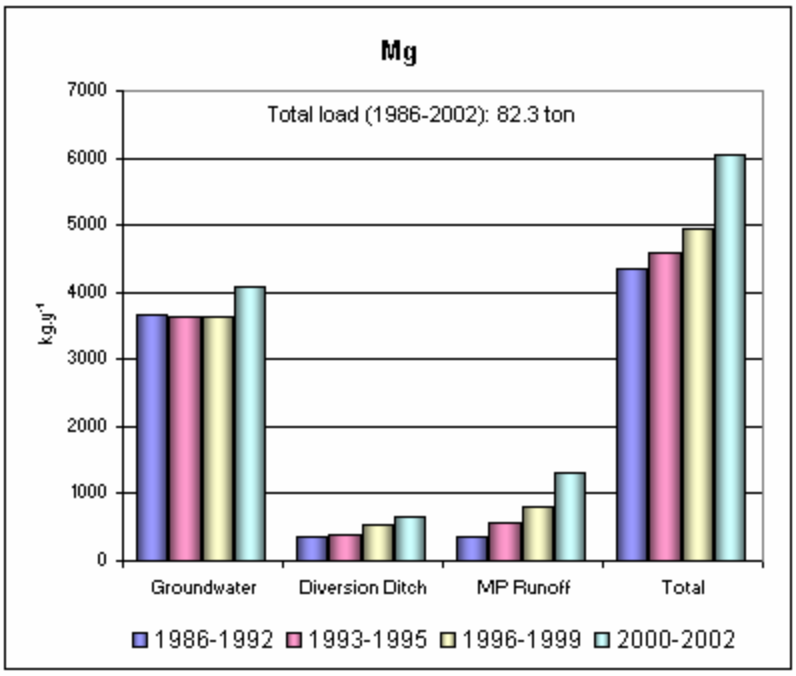


Figure 9: Changes in water [Mg] over time in Boomerang Lake

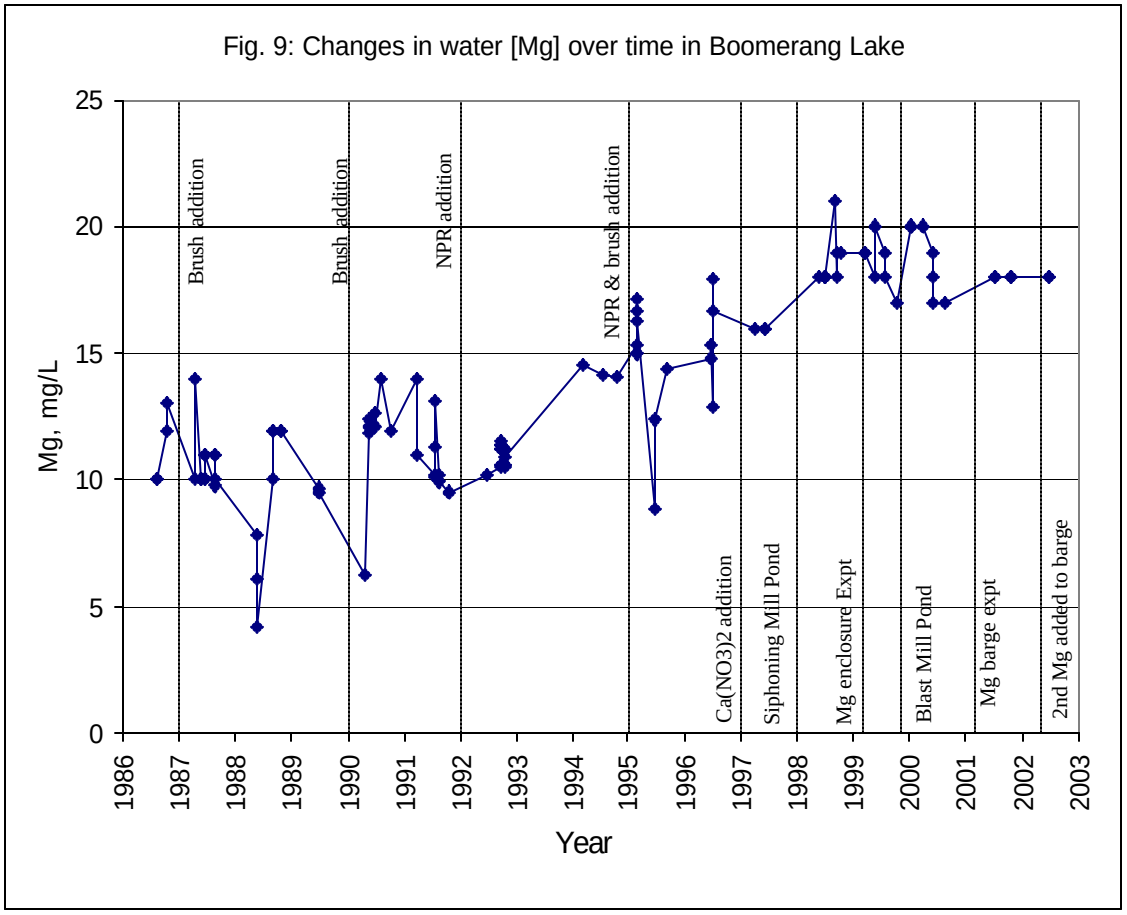


Plate 11: Mg placement in Backfill Raise 2003

Plate 12: Mg placement in WHS 2000

Conclusions

The effectiveness of Boomerang Lake as a biological polishing pond is dependent on the ability of the biomass in it to sequester metals and the capacity of its sediment to retain them. Metals incorporated into organic sediments and stabilized under reducing conditions (anoxic) transform back into metal sulfides through the action of microbial consortia and will remain in the sediments as long as they are not disturbed (Kalin et al. 1997; Kalin 1992; Kalin and Caetono Chaves 2003). Sediment dynamics and, in particular, the cycle of solubilisation and precipitation of metals in them are currently being studied.

This report addresses the behavior of the incoming metal and its retention within the lake. Clearly, the phosphate and brush additions have been beneficial. The proliferation of both benthic (bottom-growing) moss and algae, which stabilize the underlying sediment, are probably helping to stabilize the pH values in the lake. Not considered in this report is the effect of wetlands, developed at the outflow, to further polish the water. (Plates 13 and 14).

Plate 13: Cut brush in outflow 1988

Plate 14: Moss growing on brush outflow 2000

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Not considered in this report are the results of an ongoing pilot-scale project at the SBWMA into the generation of alkalinity by microbes in-situ in groundwater seepages (Lau et al. 2001) or the development of wetlands at the Boomerang Lake outflow to further polish the water (Plates 13 and 14). Moreover, when the pH level of the lake has been increased to a value of 4, through applications of manganese, phytoplankton productivity will increase, further enhancing the effectiveness of the lake as a polishing system. All these initiatives, when fully implemented, will continue to preserve the water quality of Confederation Lake, currently well within provincial standards. (MOE).

A major objective of the work at South Bay, since the start of the project in 1985, has been to identify, correct, and if possible, eliminate the sources of contamination on the site through applications of Ecological Engineering. All measures taken at the site initially implemented as small-scale tests, both on the site and in the laboratory, and scaled up through pilot demonstrations before full implementation. The goal of all the work has been to reduce the contaminant flow and increase the polishing capacity of the lake to the point until the two are in equilibrium. The data clearly indicates that this is an achievable goal. The work at South Bay demonstrates that Ecological Engineering offers an economical and environmentally benign remedy for AMD.

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